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(54) METHOD FOR REMOVING DISSOLVED OXYGEN USING HYDROGEN ACTIVATED BY CONDUCTOR SURFACE

(57)Abstract:

PURPOSE: To make it possible to preserve various kinds of drinks over a long period of time by putting a water-insoluble conductor into an aq. soln. and applying electric energy and/or vibration energy to the conductor while blowing gaseous hydrogen thereto to activate the hydrogen, thereby changing and removing the dissolved oxygen in the aq. soln.

CONSTITUTION: This method for removing the dissolved oxygen to be executed in order to preserve the drinks, such as juice and milk, over a long period of time or to suppress the corrosion of the metallic parts of boilers, steam, etc., comprises first arranging a gaseous hydrogen blowing device and the water- insoluble conductor near this device into the aq. soln. The gaseous hydrogen is blown into the aq. soln. while the electric energy or/and vibration energy is applied thereon and is brought into reaction with the dissolved oxygen in the aq. soln. by which the dissolved oxygen is rapidly removed as the water.

Water-insoluble metals, carbon or metal oxide is used for the conductor and gold, silver, platinum, palladium, etc., which are nobler in ionization tendency than hydrogen are used in the case only the vibration energy is applied on the aq. soln.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention puts in the conductor of water-insoluble nature into solution, and relates to the method of removing the oxygen which blows hydrogen gas into this, is activated to it, and is dissolved in it. Although it is, it can consider as circulating water which can save a drink over a long period of time if it applies to drinks, such as beer, fruits, vegetable juice, tea, and cow's milk, as solution, will be made to a thing harmless to a human body if it applies to tap water as solution, and suppresses the corrosion of metal parts, such as a boiler and steam. The material of a conductor can be chosen from the oxide of the metal of water-insoluble nature, carbon, or a metal. Since it dissolves and it sticks to a conductor front face, a part of hydrogen blown into solution is activable if the energy of both electrical energy, vibrational energy, or ***** is added to a conductor, and it reacts with dissolved oxygen, and this changes it to water, and can remove it. Depending on the kind of conductor, and the energy to add, consecutive processing is possible, and the utility value on industry is large. Since unreacted hydrogen can carry out the cyclic use of waste water, a part for the amount dissolved in solution, the dissolved oxygen, and the equivalent which reacts chemically is sufficient for the initial complement, and it is very economical.

[0002]

[Description of the Prior Art] Although the oxygen which dissolved in solution is the important matter which should not be lacked required for the living thing which survives underwater, when it leaves for the viewpoint which saves without deteriorating an object over a long period of time, or is not made to corrode a metal, or is said, it is the detrimental matter, and into tap water, the active oxygen which does damage, such as ozone and a peroxide, is dissolving in the human body, and, as for these, removing as a toxic substance is desirable. Although it was possible to have added and removed a reducing agent to this when it was a Prior art, other matter contained in a reducing agent will remain in solution, and was not desirable about especially food. Although it was also just going to be considered to blow hydrogen gas on the other hand, it was difficult not to react with dissolved oxygen but to remove in ordinary temperature, if it remains as it is. Although it was studied that a proton generates on it when platinum was made into the catalyst, reacting also in ordinary temperature and hydrogen were blown into water and there was a piece of platinum, hydrogen gas and oxygen gas blew hydrogen gas into solution, removed dissolved oxygen industrially, and were not considered to be a way etc.

[0003]

[Problem(s) to be Solved by the Invention] As what has required saving without making it deteriorate over a long period of time, "Beer was so good that it is new as a property" was said about beer, and beer was kept fresh [how] until now, or much devices have been made. Usually, quality changes under the influence of yeast, temperature, direct rays, oxygen, etc., and, as for beer, the delicate flavor of the slack draft beer of structure length and the scent are spoiled. Correspondence almost sufficient about yeast, temperature, and direct rays was made, and the appropriate effect has been obtained. If the mailer NOJIN coloring matter contained in beer oxidizes, a color will become deep, protein will oxidize, and it will combine with tannin or a bitter substance, if this exists, and oxidization progresses further about oxygen, the smell called oxidized odor will occur and flavor and a scent will fall. It is filled up with beer, changing to filling up a container for preservation at the air in a container (oxygen), and pressurizing carbon dioxide gas. however, oxygen -- ordinary temperature -- the inside of beer -- several -- carry out the mg/l dissolution, and since you were not able to do, this dissolved oxygen should make it, as for removing this, ask about the component of beer strangely by the Prior art -- it was unavoidable to spoil the flavor and a scent Moreover, since it deteriorated for a short period of time and deteriorated in the taste and the scent with the fresh thing even if it removed dissolved oxygen about fruits, vegetable juice, and cow's milk similarly, and was not considered a way etc. at all but it stuffed the container, pull-date had to be shortened. About tap water, the ozone or the peroxide used besides a certain dissolved oxygen from the first for sterilization will be contained as active oxygen, and since damage will be done to a human body when it becomes more than concentration with these, the removal method has been a problem. Moreover, since dissolved oxygen corrodes the metal part when used for circulating water, such as a boiler and steam, it is a technical problem to remove this.

[0004]

[Means for Solving the Problem] Further, although the method of this invention person making the hydrogen gas activated by the plasma state as above The means for solving a technical problems reacting with the oxygen blown in and dissolved in solution previously, and removing this was developed, even if hydrogen is not activated beforehand, after blowing it, it was made to react with the oxygen activated and dissolved by the suitable method, and could not remove this, or inquired, and completed this

invention. If hydrogen is blown into solution, a part will serve as dissolved hydrogen, and a part serves as air bubbles with a gas, and is soon carried out of a system. In addition, a part serves as a gas with time and dissolved hydrogen is also considered to maintain a kind of reversible-equilibrium state so that, as for a part, the hydrogen in air bubbles may also turn into dissolved hydrogen again. Even if the oxygen and hydrogen of **** live together in solution; in ordinary temperature, it hardly reacts. Where either or both sides is activated, if it contacts, it will react rapidly and will change to water. With the state here where it was activated, it is thought that what is necessary is just to change into ion or the state where it became radical. When electrical energy, vibrational energy, or the energy of the both sides was added having put in the specific conductor and blowing hydrogen gas into solution, as a result of examining many things, temporarily, it was thought that it became radical and it was admitted for the hydrogen or oxygen of **** ion or that the oxygen of **** served as water promptly and it was removed. The conductor used for this invention is the oxide of the metal of water-insoluble nature, carbon, or a metal, and when adding only vibrational energy, an IMEN-ized inclination can use these alloys, such as gold, silver, platinum, PARAJUUMU, ROJUUMU, a ruthenium, and IRIJUUMU, as a **** metal from hydrogen. Even if it is **, since copper, mercury, etc. serve as a toxic substance when the minute amount dissolution is carried out and it is especially aimed at a drink in water, they are not more desirable than hydrogen. In an ionization tendency, from hydrogen, I hear that the direction of hydrogen tends to become ion, and ** has it, when a hydrogen overvoltage is small and hydrogen contacts a metal. Therefore, if the hydrogen and oxygen of **** stick to a surface of metal, hydrogen ionizes, and a metal will be charged in minus, will give the electrical and electric equipment to the oxygen which the electron moved and adsorbed the inside of a metal, and will serve as an anion at a proton. The proton of hydrogen and the anion of oxygen join together in solution, and it becomes water and breaks away. If vibrational energy is added to a metal, secession will be promoted and a reaction will be accelerated. If especially vibration also adds supersonic oscillation energy, a hydrogen overvoltage will fall and it will become easier to ionize. 1 or more kHzs, the ultrasonic energy which affects a hydrogen overvoltage is the frequency of 10 or more kHzs preferably, and since energy efficiency falls, it is desirable in 1 or more MHzs, to add the ultrasonic wave of 10 or more kHzs the frequency of 1 or less MHz. Moreover, it is good to make it the shape of powder and a foil and porosity as a metaled configuration, so that a surface area may become large. Moreover, when a hydrogen overvoltage falls sharply, it accepts. For example, platinum plating (porosity) and the platinum black (powder) of a hydrogen overvoltage are smaller than a platinum simple substance. Moreover, plating or the thing which carried out vacuum evaporation can also use the above-mentioned metal for carbon, a ceramic, a resin, etc. as support. Although a conductor may be fixed, if it does not fix in the case of the shape of powder and a foil but enables it to flow freely to a fluid bed type, a reaction will be accelerated more. What is necessary is just to apply the voltage of a direct current or an alternating current to this, for applying electrical energy to a conductor. The oxide of the metal used for the insoluble anode other than an above-mentioned metal as a material of a conductor, carbon, or a metal can be used. That is, oxides, such as iron, a tungsten, a ruthenium, and PARAJUUMU, can be used as one sort or two sorts or more of alloys, these metals or the above-mentioned metal, such as nickel, cobalt, a tungsten, molybdenum, titanium, a tantalum, and niobium, conductive carbon, and a conductive metallic oxide. When applying the voltage of a direct current, if electric resistance is low, current will flow including an electrolyte in solution. In an anode plate, it reacts with the hydrogen to which it stuck when the hydroxide ion which the hydrogen which stuck to the front face ionized, and became a proton, and was able to be drawn near to an anode plate discharged, and water is generated. In cathode, it reacts with the oxygen to which it stuck when BURTON of the hydrogen which was able to be drawn near discharged, and water is generated. When hydrogen is blown superfluously, there is little oxygen which sticks to cathode and it is thought that the hydrogen proton which was able to be drawn near to cathode discharges, and a hydrogen radical generates most. Although this radical will serve as a hydrogen-content child if a life carries out radical comrade contact short, if dissolved oxygen is contacted, it will react immediately and will change to water. Although the voltage which should be applied is influenced very much by various kinds of conditions, such as electric resistance of a between, pH of liquid, and temperature, it is necessary to apply the above voltage which can ionize the hydrogen of this system anyway. Usually, more than 2V5-50V are a desirable voltage range. If it becomes more than 50V, a reaction secondary in addition to the reaction of hydrogen and oxygen starts [the chemical change of the component for example, in solution] and is not desirable. What is necessary is to keep one's distance and just to install some shades and positive two poles near the hydrogen entrainment mouth, in this invention. However, generally, even if electric resistance is high and a drink, tap water, etc. apply the voltage of a direct current, current does not flow easily. On the other hand, if the voltage of an alternating current, especially a RF is applied, liquid resistance will fall and current will come to flow. As frequency, 1 or more kHzs have 10 or more preferably good kHzs. Since a pole changes and it is caught by the pole before this breaks away, even if hydrogen will ionize with much trouble, if frequency becomes very high, it becomes the same thing as not applying voltage seemingly, and an effect is not accepted. If it becomes especially a RF, the speed from which the male and female principles of an electrode changes will become large too much, and it will become impossible to diffuse ion, although it is also one means to raise the rate of flow on the front face of an electrode, and to enlarge the diffusion rate of ion. Therefore, ion can be diffused if the vibrational energy of larger frequency than the frequency from which the male and female principles of an electrode changes is added. Since 1 or less MHz is desirable as mentioned above, the frequency of the vibrational energy still added should also make voltage of a RF 1 or less MHz. Thus, into the solution which put in the conductor, if hydrogen gas is blown adding vibrational energy, electrical energy, or its both sides, the dissolved acid quantum in solution can decrease gradually, and, finally can set it to 0. On the other hand, a dissolved acid quantum hardly changes only by blowing hydrogen gas into water. With the solution of this invention, the matter of a solid-state, a liquid, and a gas is dissolved in water. Moreover, with dissolved oxygen, what was dissolved into solution liquid as active oxygen, such as molecule oxygen, ozone, or ion, is included. If the kind, the electrical energy to apply, and vibrational energy of a conductor are chosen suitably, processing continuously is

possible and industrial value is large.

[0005]

[Function] In this invention, it is thought on a conductor front face that the following reactions start.

(1) Anode plate : protonation of the hydrogen-content child who stuck to $H_2 \rightarrow 2H^+ \rightarrow 2e^-$ or $2OH^- + H_2 \rightarrow 2H_2O + 2e^-$, i.e., an anode plate, and the generation reaction of the water by the electric discharge of OH^- ion which was able to be drawn near, and an adsorption hydrogen-content child's reaction start. However, at the time of a hydrogen entrainment, the hydrogen-content child is doing abundant adsorption at the anode plate, OH^- ion with large volume cannot approach an anode plate easily, and protonation of hydrogen serves as a main reaction.

(2) Cathode : $2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O$ Or electric discharge of the hydrogen proton which was able to be drawn near to $2H^+ \rightarrow 2H$ and $+2e^-$, i.e., cathode, generation of the water by the reaction of the oxygen-content child who adsorbed, and generation of the hydrogen radical by electric discharge of the above-mentioned proton start. However, the hydrogen proton generated by (1) at the time of a hydrogen entrainment can draw near to abundant cathode, and since it is very much hard to stick to the oxygen with large volume, generation of a hydrogen radical serves as a main reaction. Therefore, hydrogen IMEN and a hydrogen radical occur in the offing of an electrode. Since a hydrogen ion can be soon drawn near to cathode and carries out the reaction of the above (2), the hydrogen radical will generate it as a main reaction seemingly after all. although the reaction of the above (1) and (2) starts momentarily when the voltage of an alternating current is applied, since an electrode is alike by turns and changes, a hydrogen proton will be in the state where it hardly moves, and a hydrogen radical will generate it too Thus, the generated hydrogen radical reacts with dissolved oxygen, and generates water.

$2H\text{and} + O_2 \rightarrow 2OH^-$ Contact of $2OH^-$, $+2H\text{and} \rightarrow 2H_2O$ however H , and a comrade extinguishes a radical soon by the following termination reaction.

When not applying $H-H \rightarrow H_2$ (3) electrical energy, as for the hydrogen-content child who stuck to the front face when it was **, the ionization tendency of a conductor tends to ionize from hydrogen, hydrogen is carried out at plus and a conductor carries out electrification polarization at minus. If the oxygen-content child dissolved in solution sticks to a conductor, an oxygen-content child will get the electrical and electric equipment of minus from a conductor, and will be charged as an oxygen anion. The hydrogen plus ion and oxygen anion which were charged here carry out joint electric discharge with ***** on a conductor front face, serve as a moisture child, and break away from a conductor front face. Under the present circumstances, if it is especially alike and the energy of an ultrasonic wave is added, since it will become easy to polarize and diffusion of ion and a molecule will become large again, the above-mentioned reaction is sharply accelerable. By the way, it is thought of for a radical's generating as follows according to autoxidation, and oxidizing the organic compound of the contents that the dissolved oxygen in a drink carries out deterioration degradation of the organic compound (RH) of contents.

$RH \rightarrow R\text{and} + H^-$ (initiation reaction)

$R^- + O_2 \rightarrow RO_2^-$ $RO_2\text{and} + RH \rightarrow ROOH + R^-$ (propagation)

$2RO(s)$ and $\rightarrow ROOR$ (termination reaction)

In this case, it returns to the compound RH of even if it reacts with the radical and oxide which H^- generated in this invention is generating by the above-mentioned reaction, and oxidization is stopped.

RO_2^- , $+5H$, and $\rightarrow RH + 2H_2O$ $ROOH + 3H\text{and} \rightarrow R^- + 2H_2O$ $ROOR + 4H\text{and} \rightarrow 2R^- + 2H_2O$ Although $R^- + H^- \rightarrow RH$ and dissolved hydrogen cannot return $ROOH$ and $ROOR$ easily, they are considered that it may react and may return to RH with RO_2^- and a radical.

Since the amount of dissolved hydrogen will increase in proportion to a pressure if it can be made pressurization when blowing RO_2^- , $+2H_2 \rightarrow ROH$, $+H_2O \rightarrow ROH$, and $+2H_2 \rightarrow 2RH + 2H_2O$, in addition hydrogen, the removal reaction of dissolved oxygen is accelerable.

[0006]

[Example]

Gold was made into thickness and what carried out about 0.12micro machine plating was used for the hollow polyester ball whose 1st example diameter is 10mm as a conductor. 360mm height filled [content volume] up with about 21% the pressurized container made from stainless steel which is 200l. for the above-mentioned ball by 2000mm at the 80000-piece occupied volume, and the diameter designed so that the ultrasonic wave of 12kW of oscillation frequency 36kHz outputs could be applied to this. Solution was passed from the upper part in this container, hydrogen gas was blown from the lower part, and the cyclic use of waste water of the hydrogen which passed through the inside of solution and escaped in the upper part was carried out so that it might blow in again using a pump. Five sets of this container were put in order in series, and the solution processed with the container to begin was connected in the pipe, and was used as the **** processor so that it could process similarly with the following container. In order to measure the elimination factor of the dissolved oxygen in solution, the sample tap was attached in the pipe of the outlet of each container, and the dissolved acid quantum was measured. In order to remove the dissolved oxygen of the beer which digestion ended using above equipment, it processed on condition that the following. The following are the conditions for every container.

Beer rate of flow: 0.8kl/min.

Hydrogen entrainment: Flow rate: 12l-kg/cm2/min. Pressure: 1.8 kg/cm2 ultrasonic-wave oscillation: 36kHz 12kW beer solution temperature : After performing such [0.5 degrees C] processing continuously and being in a steady state, when the dissolved oxygen concentration of the outlet of each containers 1, 2, 3, 4, and 5 was measured, the result shown in Table 1 was obtained.

表1 各容器出口の溶存酸素濃度

酸素濃度測定箇所	酸素濃度 (mg/l)
熟成終了直後(処理前)	1.24
容器1出口	0.45
容器2出口	0.18
容器3出口	0.07
容器4出口	0.03
容器5出口	0.00

In the above, an oxygen density is set to about 0 and can save fresh beer now over a long period of time at the outlet of a container 5.

[0007] It processed by connecting the container of the 1st above-mentioned example with a three-set serial so that removal of dissolved oxygen could do continuously tap water which carried out sterilization processing using the 2nd example ozone. The path of a circle enlarges from 80mm what considered as the conductor and galvanized about 0.25micro of PARAJUUMU at the wire gauze (200 meshes) of titanium every 20mm at a cylindrical shape with a height of 1.8m, and they are 100mm, 120mm, 140mm, It built in size of 280mm, 300mm, and 320mm, and these were installed into the above-mentioned container in the shape of a concentric circle so that the distance between wire gauzes might be set to 10mm. The pillar object of each wire gauze is connected and enabled it to conduct current by the titanium line which carried out PARAJUUMU plating. Hydrogen sandwiched non-**** of RIIRON between circle prism ***** so that it might contact at the wire gauze at which it blows in from the bottom center section of the container, and the foam of hydrogen serves as an electrode well. The wire gauze in a container and the volume pulse duty factor of a nylon nonwoven fabric were 18.6%. The above-mentioned tap water was poured from the container upper part, hydrogen was blown from the container pars basilaris ossis occipitalis, and unreacted hydrogen carried out collection cycle use. It was made to be possible [with a pipe / consecutive processing of each container] like the 1st example. The sample tap was attached in the pipe of each container outlet, and dissolved oxygen concentration was measured. The conditions for every container of dissolved deoxidation consecutive processing of tap water are the followings.

Tap water rate of flow : 0.24kl/min.

Hydrogen entrainment: Flow rate: 10.8l-kg/cm2/min. Pressure: 1.

2 kg/cm2 Ultrasonic oscillation : 28kHz and 12kW Electrode grant power: 10kHz, 10V, and 2.1**0.6A -- such processing was performed continuously, and after being in a steady state, when the dissolved oxygen concentration of the outlet of each containers 1 and 2 and 3** was measured, the result shown in Table 2 was obtained

表2 各容器出口の溶存酸素濃度

酸素濃度測定箇所	酸素濃度 (mg/l)	オゾン濃度 (mg/l)
処理前	11.80	2.25
容器1出口	3.34	0.08
容器2出口	0.86	0.00
容器3出口	0.00	0.00

※ 酸素濃度の測定値にはオゾン濃度も含まれる

As mentioned above, at the outlet of a container 3, an oxygen density and an ozone level are set to about 0, and can consider as tap water harmless to a human body by this processing.

[0008]

[Effect of the Invention] Since most dissolved oxygen concentration can be set to 0 by this method in beer as shown in the 1st example of an example, it is lost that the flavor of beer and a scent deteriorate by oxygen, and it can save over a long period of time by putting the freshness in a container. Moreover, similarly, fruits, vegetable juice, tea, cow's milk, etc. can remove the dissolved oxygen which was untouched conventionally, and can offer the mothball method of the freshness which was superior to before much more. As shown in the 2nd example of an example, in tap water, dissolved ozone detrimental to a human body is removable, and since dissolved oxygen is almost 0, this water can suppress metaled corrosion, and the life of the metal device which uses hot circulating water, such as a boiler and steam, especially can be lengthened more. As the example showed, hydrogen can carry out the cyclic use of waste water, and the consumption ends with few [dissolved oxygen, the amount which reacts theoretically, and the amount dissolved in solution] amounts and is economical. Moreover, since it can process continuously, the utility value on the industry is large.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The removal method of the dissolved oxygen using the hydrogen activated on the conductor front face which the conductor of water-insoluble nature is put in into solution, and you activate [removal method] the hydrogen which added the energy of these both sides to the conductor by electrical energy or vibrational energy, and the case, was blown into it, and stuck to the conductor front face, blowing hydrogen gas into this, makes it react with the dissolved oxygen in solution, and changes this to water.

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(54) 【発明の名称】 導電体表面で活性化した水素を用いた溶存酸素の除去法

(57) 【要約】

【目的】 この発明は水溶液中に水不溶性の導電体を入れ、これに水素ガスを吹き込みつつ導電体に電気エネルギー又は振動エネルギー乃至その双方のエネルギーを加えて、吹き込まれた水素を活性化し、水溶液中の溶存酸素を水に変化させて除去するためのもので、これによってビール、果実や野菜のジュース、茶、牛乳等の飲料に適用すれば、これらを長期間にわたって変質させないで保存することができる。また水道水に適用すれば人体に有害なオゾン、活性酸素等が除去されて無害化することができ、ボイラー、スチーム等ではこの水を循環水に使用すれば腐食が抑制されその耐久性を延ばすことができる。

【構成】 水溶液中に水素ガスを吹き込み器とその近傍に水不溶性の導電体を設置し、これに電気エネルギー又は振動エネルギー乃至その双方のエネルギーを加えつつ水素ガスを吹き込み水溶液中の溶存酸素と反応させる。

(2)

特開平9-1153

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【特許請求の範囲】

【請求項1】 水溶液中に水不溶性の導電体を入れ、これに水素ガスを吹き込みつつ導電体に電気エネルギー又は振動エネルギー、場合によりこれら双方のエネルギーを加えて、吹き込まれて導電体表面に吸着した水素を活性化し、水溶液中の溶存酸素と反応させこれを水に変化させる、導電体表面で活性化した水素を用いた溶存酸素の除去法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は水溶液中に水不溶性の導電体を入れ、これに水素ガスを吹き込んで活性化し溶存する酸素を除去する方法に関するものであるが、水溶液としてビール、果実、野菜のジュース、茶、牛乳等の飲料に適用すれば飲料を長期間にわたって保存でき、水溶液として水道水に適用すれば人体に有害なものにでき、またボイラー、スチーム等の金属部分の腐食を抑制する循環水とすることができる。導電体の材料は水不溶性の金属、炭素あるいは金属の酸化物から選ぶことができる。水溶液中に吹き込まれた水素は一部溶解して導電体表面に吸着するので、導電体に電気エネルギー又は振動エネルギー、乃至はこれら双方のエネルギーを加えると活性化することができ、これが溶存酸素と反応して水に変化させて除去できる。導電体の種類、加えるエネルギーによっては連続処理が可能であり産業上の利用価値は大きい。未反応の水素は循環使用できるので、その必要量は水溶液中に溶解する量と溶存する酸素と化学的に反応する当量分で足りきわめて経済的である。

【0002】

【従来の技術】 水溶液中に溶解した酸素は例えば水中に生存する生物にとっては必要欠くべからざる重要な物質であるが、物を長期間にわたって変質させないで保存するとか、金属を腐食させないとかいう観点になつと有害な物質であり、また水道水中には人体に害を及ぼすオゾン、過酸化物質等の活性酸素が溶解しており、これらは有害物質として除去することが好ましい。従来の技術であればこれに還元剤を加えて除去することは可能であるが、還元剤に含まれる他の物質が水溶液中に残存することになり、特に食品品に関しては好ましいことではなかった。一方水素ガスを吹き込むことも考えられるところであるが、常温でそのままでは溶存酸素と反応せず除去することは困難であった。水素ガスと酸素ガスは白金を触媒とすると常温でも反応すること、又水素を水の中に吹き込む場合白金片があるとその上でプロトンが生成することが研究されていたが、水素ガスを水溶液中に吹き込んで工業的に溶存酸素を除去しようなどとは考えられていなかった。

【0003】

【発明が解決しようとする課題】 長期間にわたって変質させないで保存することが必要なものとして、例えばビ

2

ールに関しては「ビールは性質として新しいほど良い」といわれ、これまでにビールを如何に新鮮に保つか数々の工夫がなされてきた。通常ビールは酵母、温度、直射日光、酸素等の影響で品質が変化し、つくりたての樽生ビールの微妙な風味、香りが損なわれていく。酵母、温度、直射日光等についてはほとんど十分な対応がなされ、それなりの効果をあげてきた。酸素については、これが存在するとビールに含まれるメラノジン色素が酸化されて色が濃くなり、タンパク質が酸化されてタンニンや苦味物質と結合したりして、更に酸化が進むと酸化臭とよばれる臭いが発生して風味、香りがおちてくる。保存のため容器に充填するには容器内の空気（酸素）に換えて炭酸ガスを加圧したままビールを充填している。しかし酸素は常温でビール中に数mg/l溶解しており、これを除去することは従来の技術ではできなかったの。この溶存酸素がビールの成分を変質させその風味、香りを損なうことは止むを得ないことであった。また同様に果実、野菜ジュース、牛乳等についても溶存酸素を除去しようなどとは全く考えられておらず、容器に詰めても短期間で変質し、新鮮なものとは味、香りにおいて劣化してくるので賞味期間を短くせざるをえなかった。水道水についてはもとよりある溶存酸素の他に、殺菌のため用いられたオゾンあるいは過酸化物質が活性酸素として含まれることになり、これらがある濃度以上になると人体に害を及ぼすことになるので、その除去法が問題になっている。またボイラー、スチーム等の循環水に用いられる場合溶存酸素がその金属部分を腐食するのでこれを除去することが課題である。

【0004】

【課題を解決するための手段】 本発明者は先に上記のような課題を解決するための手段として、プラズマ状態で活性化した水素ガスを水溶液中に吹き込んで溶存する酸素と反応させこれを除去する方法を開発したが、更に水素は予め活性化しなくとも、吹き込んだ後適当な方法で活性化して溶存する酸素と反応させこれを除去できないか研究を行い本発明を完成させた。水溶液中に水素を吹き込むと一部は溶存水素となり、一部は気体のまま気泡となりやがて系外に持ち出される。なお溶存水素も時間と共に一部は気体となり又気泡中の水素も一部は溶存水素となるように一種の可逆平衡状態を保っていると考えられる。水溶液中に溶存の酸素及び水素が共存しても常温ではほとんど反応しない、どちらか又は双方が活性化した状態では接触すると急激に反応して水に変化する。ここでいう活性化した状態とはイオン又はラジカルになった状態にすればよいと考えられる。種々検討した結果、水溶液中に特定の導電体を入れ水素ガスを吹き込みつつ電気エネルギーあるいは振動エネルギー乃至その双方のエネルギーをくわえると、溶存の水素あるいは酸素が一時的にイオン又はラジカルになると考えられ、溶存の酸素が速やかに水となって除去されることが認められ

(3)

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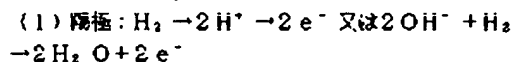
た。本発明に用いる導電体とは水不溶性の金属、炭素あるいは金属の酸化物で、振動エネルギーのみを加える場合にはイメニ化傾向が水素より貴な金属として金、銀、白金、パラジウム、ロジウム、ルテニウム、イリジウム等乃至これらの合金を用いることができる。水素より貴であっても、銅、水銀等は水に微量溶解し、特に飲料を対象とした場合有害物質となるので好ましくない。イオン化傾向が水素より貴ということは水素過電圧が小さく金属に水素が接触した場合、水素の方がイオンになり易いということである。従って金属表面に溶存の水素と酸素が吸着すると、水素がイオン化してプロトンに、金属はマイナスに帯電して金属中を電子が移動して吸着した酸素に電気を与えアニオンとなる。水溶液中で水素のプロトンと酸素のアニオンが結合して水となって離脱する。金属に振動エネルギーを加えれば離脱が促進され反応が加速される。振動でも特に超音波振動エネルギーを加えると水素過電圧が下がってよりイオン化し易くなる。水素過電圧に影響を与える超音波エネルギーは1kHz以上好ましくは10kHz以上の周波数で、1MHz以上ではエネルギー効率が下がるので、10kHz以上1MHz以下の周波数の超音波を加えることが好ましい。又金属の形状としては、表面積が大きくなるよう粉末状、箔状、多孔質にすると良い。又水素過電圧が大幅に下がる場合も認められている。例えば白金単体よりは白金めっき（多孔質）、白金黒（粉末）の方が水素過電圧が小さい。又担体として炭素、セラミック、樹脂等上記金属をめっき乃至蒸着させたものも使用できる。導電体は固定してもよいが、粉末状、箔状の場合は固定せず流動層型に自由に流動出来るようにしておけば反応はより加速される。導電体に電気エネルギーを加えるにはこれに直流又は交流の電圧を加えればよい。導電体の材料としては上述の金属の他に不溶性電極に用いられる金属、炭素或いは金属の酸化物が使用できる。即ちニッケル、コバルト、タンゲステン、モリブデン、チタン、タantal、ニオブ、等、或いはこれら金属と上述金属の1種又は2種以上の合金、導電性の炭素、又導電性金属酸化物として鉄、タンゲステン、ルテニウム、パラジウム等の酸化物を使用することが出来る。直流の電圧を加える場合、水溶液中に電解質を含み電気抵抗が低いと電流が流れる。陰極では表面に吸着した水素がイオン化してプロトンとなり、又陽極に引き寄せられた水酸イオンが放電する際に吸着した水素と反応して水を生成する。陰極では引き寄せられた水素のプロトンが放電する際に吸着した酸素と反応して水を生成する。水素が過剰に吹き込まれている場合には陰極に吸着する酸素は少なく殆どは陰極に引き寄せられた水素プロトンが放電して水素ラジカルが生成すると考えられる。このラジカルは寿命が短くラジカル同志接触すれば水素分子となるが、溶存酸素と接触すれば直ちに反応して水に変化する。加えるべき電圧は極間の電気抵抗、液のpH、温度

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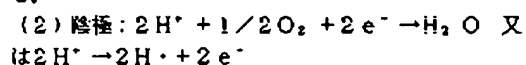
等各種の条件に影響されるが、いずれにしてもこの系の水素がイオン化できる以上の電圧を加える必要がある。通常2V以上5～50Vが好ましい電圧範囲である。50V以上になると水素と酸素の反応以外に副次的な反応が、例えば水溶液中の成分の化学変化がおこって好ましくない。本発明においては水素吹き込み口近傍に陰、陽電極を少し距離をおいて設置すればよい。但し一般的に飲料、水道水等は電気抵抗が高く直流の電圧をかけてもなかなか電流が流れない。これに対して交流特に高周波の電圧をかけると、液抵抗が下がって電流が流れるようになる。周波数としては1kHz以上好ましくは10kHz以上がよい。周波数が非常に高くなると水素が折角イオン化してもこれが離脱する前に極が変わって極に捕獲されるので見かけ上電圧をかけないのと同じこととなって効果認められない。電極表面の流速を上げてイオンの拡散速度を大きくするのも一つの手だてであるが、特に高周波になると電極の陰陽が変化する速度が大きくなりすぎてイオンが拡散できなくなってしまう。そのために電極の陰陽が変化する周波数より大きい周波数の振動エネルギーを加えるとイオンが拡散できるようになる。それでも加えられる振動エネルギーの周波数は上述のように1MHz以下が好ましいので、高周波の電圧も1MHz以下にすべきである。このようにして導電体を入れた水溶液中に水素ガスを振動エネルギー又は電気エネルギー乃至その双方を加えながら吹き込むと、水溶液中の溶存酸素量は次第に減少し最後には0にすることができる。これに対して水素ガスを水に吹き込んだだけでは溶存酸素量はほとんど変化しない。本発明の水溶液とは水に固体、液体、気体の物質を溶解したものである。また溶存酸素とは分子酸素、オゾン、あるいはイオン等の活性酸素として水溶液中に溶解したものを含む。導電体の種類、加える電気エネルギー及び振動エネルギーを適当に選べば連続的に処理することが可能であり産業的価値は大きい。

【0005】

【作用】本発明において導電体表面では以下の反応がおこると考えられる。



即ち陰極に吸着した水素分子のプロトン化及び引き寄せられたOHイオンの放電と吸着水素分子の反応による水の生成反応がおこる。但し水素吹き込み時には陰極には水素分子が多量吸着しており、体積の大きいOHイオンは陰極に寄りにくく、水素のプロトン化が主反応となる。



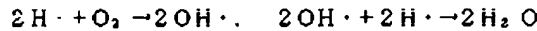
即ち陰極に引き寄せられた水素プロトンの放電と吸着した酸素分子の反応による水の生成と上記プロトンの放電による水素ラジカルの生成がおこる。但し水素吹き込み

(4)

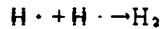
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時には(1)で生成した水素プロトンが多量陰極に引き寄せられ、体積の大きい酸素はなかなか吸着しにくいので水素ラジカルの生成が主反応となる。従って電極の沖合では水素イオンと水素ラジカルが発生してくる。水素イオンはやがて陰極に引き寄せられて上記(2)の反応をするので結局は水素ラジカルが見かけ上主反応として*

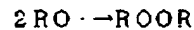
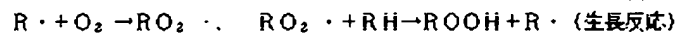
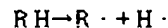


但しH・同士が接触すると、下記の停止反応でラジカルはやがて消滅する。



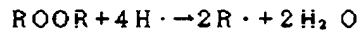
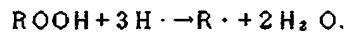
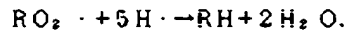
(3)電気エネルギーを加えめ場合

導電体のイオン化傾向が水素より貴であればその表面に吸着した水素分子はイオン化する傾向にあり、水素はプラス、導電体はマイナスに帯電分極する。水溶液中に溶存する酸素分子が導電体に吸着すると酸素分子は導電体からマイナスの電気をもらって酸素マイナスイオンとし※

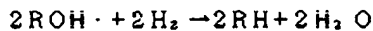


この場合本発明において生成したH・が上記反応により20★物RHに還元し酸化を停止させる。

生成しているラジカル及び酸化物と反応してもとの化合物★



また溶存水素はROOH、ROORは還元しにくいR₂O₂・ラジカルとは反応してRHに還元する可能性はあると考えられる。



なお水素を吹き込む場合加圧にすることができれば溶存水素量が圧力に比例して増えるので溶存酸素の除去反応を加速することができる。

【0006】

【実施例】

第1例

直径が10mmの中空ポリエステルボールに金を厚みにして約0.12μ機械めっきしたものを導電体として用いた。直径が360mm高さが2000mmで内容積が200lのステンレス製の圧力容器に上記ボールを80000個占有体積で約21%を充填し、これに共振周波数36kHz出力12kWの超音波をかけられるよう設計した。この容器に上部から水溶液を流し、下部から水

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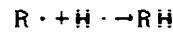
*生成していることになる。交流の電圧をかけた場合には瞬間的には上記(1)、(2)の反応がおこるが電極が交互に変わるので水素プロトンはほとんど動かない状態になり、やはり水素ラジカルが生成することになる。このようにして生成した水素ラジカルは溶存酸素と反応して水を生成する。

※で帯電する。ここで帯電した水素プラスイオンと酸素マイナスイオンが導電体表面で近づくことと結合放電して水分子となって導電体表面より脱離する。この際に特に超音波のエネルギーを加えると、分極し易くなり又イオン及び分子の拡散が大きくなるので上記の反応を大幅に加速することができる。ところで飲料中の溶存酸素が内容物の有機化合物(RH)を変質劣化させるのは、自動酸化により下記のようにラジカルが生成して内容の有機化合物を酸化していくためと考えられる。

(開始反応)

(生長反応)

(停止反応)



素ガスを吹き込み、水溶液中を通過して上部に逃げた水素はポンプを用いて又吹き込むよう循環使用した。この容器を直列に5基並べ、始めの容器で処理された水溶液は次の容器で同様に処理できるようパイプでつなげて連屑処理装置とした。水溶液中の溶存酸素の除去率を測定するために各容器の出口のパイプに試料採取口を取り付け溶存酸素量を測定した。熱成の終了したビールの溶存酸素を上記の装置を用いて除去するために下記の条件で処理を行った。下記は各容器毎の条件である。

ビール流速: 0.8kl/min.

水素吹き込み: 流量: 12l・kg/cm²/min. 圧力: 1.8kg/cm²

超音波発振: 36kHz, 12kW

ビール液温: 0.5℃

このような処理を連続して行い定常状態になった後、各容器1、2、3、4、5の出口の溶存酸素濃度を測定したところ表1に示す結果がえられた。

